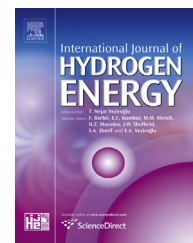




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Manganese oxides supported on nano-sized metal oxides as water-oxidizing catalysts for water splitting systems: 1-synthesis and characterization

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ABSTRACT

Water splitting to produce H₂ is an important procedure for the conversion of intermittent energies. However, the reaction is energetically limited by the water-oxidation process. Herein, we report the synthesis of Mn oxide on nanoparticles of KAl₃(SO₄)₂(OH)₆, Co₃O₄, CuO, Fe₃O₄, MgO, NiO, SiO₂, SnO₂, TiO₂, WO₃, zeolite, ZnO and ZrO₂ by a simple, low-cost and green procedure aiming at obtaining a good water-oxidizing catalyst. The obtained materials are characterized by high-resolution transmission electron microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray diffraction studies.

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Introduction

Mn oxides are flexible, with a wide diversity of structures and can be prepared with different defects, morphology, porosity and textures, low-cost and environmentally friendly with different applications in different areas [1–7], especially regarding the energy issue concerns. They can also act as supercapacitors [8,9], as catalysts in water oxidation [10–15] and they find applications in batteries [16–18]. Specific bulk

and surface structures of Mn oxides could assist the occurrence of multi-electron and complicated reactions [19,20]. In addition to bulk, they can also be used in supported, colloidal and nano-sized forms with high surface areas [21–24]. Different facile methods are available for their synthesis in pure form or in combination with other compounds. Such nanocomposites are very promising to be used in different applications [23]. However, a few groups reported on an impregnation method to synthesize such compounds [23]. In the procedure, a mixture of manganese(II) nitrate, water and

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support was heated to 343 K under continuous stirring and was evaporated to dryness. Such methods can easily lead to a mixture of Mn oxide and support instead of Mn oxide fixed on a support.

Herein, in a systematic study, we report the effect of support on the water-oxidizing activity of amorphous Mn oxides. Thus, Mn oxide on nanoparticles of $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, Co_3O_4 , CuO , Fe_3O_4 , MgO , NiO , SiO_2 , SnO_2 , TiO_2 , WO_3 , zeolite, ZnO or ZrO_2 was synthesized by a new, simple procedure and characterized by high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and Fourier transform infrared spectroscopy (FTIR). Subsequently and in the next papers, electrochemical properties and the water-oxidizing activities of these compounds are considered in the presence of Ce(IV) .

Experimental

Material and methods

All reagents and solvents were purchased from the commercial sources and were used without a further purification. Nano-sized metal oxides were purchased from the Neutrino Company. SEM images were taken with a REM JEOL JSM-7500F device. For HRTEM and TEM, samples were placed on copper grids covered with carbon film and examined with a 300 keV Transmission electron microscope JEM-3010 UHR (JEOL Ltd., Japan), equipped with a retractable high-resolution slow-scan CCD-Camera (Gatan Inc., USA) with GOS phosphorous scintillator and lanthanum hexaboride cathode as the electron source, respectively. FTIR spectra of KBr pellets of compounds were recorded on a Bruker vector 22 in the range between 400 and 4000 cm^{-1} (maximum resolution: 2.00 cm^{-1}). The X-ray powder patterns were recorded with a Bruker D8 ADVANCE diffractometer (CuK_α radiation). Mn atomic absorption spectroscopy (AAS) was performed on an atomic absorption spectrometer Varian Spectra AA 110. Prior to the analysis, the compounds were added to 1 mL of concentrated nitric acid and H_2O_2 , left at room temperature for at least 1 h to ensure that the oxides were completely dissolved. The solutions were then diluted to 25.0 mL and analysed by AAS.

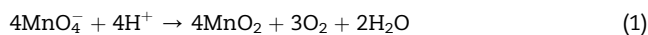
Synthesis

A solution of KMnO_4 (200 mg in 60 mL water) was added to oxides (2.00 g) and the mixture was placed under hydrothermal conditions at $120\text{ }^\circ\text{C}$ for 12 h. The solid was centrifuged and carefully washed with water to remove KMnO_4 . Then, the solid was calcined at $100\text{--}600\text{ }^\circ\text{C}$.

Results and discussion

Mn oxide/support combinations were obtained by a low-cost, simple and green method. The mechanism of Mn oxide formation on the surface of supports is not known, but the $-\text{OH}$ groups on the surface of metal oxides may induce the decomposition of the MnO_4^- ions and in the next step nano-

sized MnO_x precipitates deposit slowly on the surface of the supports (Eq. (1)) [24]:



For the redox-active supports, the oxidation/reduction reaction may form Mn oxide on the surface of the supports. The method has some advantages compared to the previously reported method:

- In the method, a thin layer of Mn oxides forms on the surface of support and mixing of Mn oxide and support is not observed under the applied conditions.
- The method is simple and is a one-step procedure.
- The method can be performed for many supports.
- The method is reproducible.
- The method can be applied in different pH.

As detected by AAS, the amounts of Mn oxides on the surface of each support are different, from 3.1% (Fe_3O_4) to 0.23% (SiO_2) (Fig. 1).

The surface of SiO_2 is too inert to react with MnO_4^- and form Mn oxide, but the redox-active supports such as Co_3O_4 and Fe_3O_4 , which can reduce MnO_4^- to MnO_x , are among supports with the highest load of Mn.

HRTEM images for Mn oxide supported on $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, Co_3O_4 , CuO , Fe_3O_4 , MgO , NiO , SiO_2 , SnO_2 , TiO_2 , WO_3 , zeolite, ZnO and ZrO_2 nanoparticles indicate the presence of amorphous Mn oxide on the surface of these crystalline supports (Fig. 2, see also [Electronic Supplementary Information](#)).

In accordance with these images, Mn oxides form a well-dispersed phase on these supports (Fig. 2a,b). In Mn oxide supported on $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ particles have cubic morphology with edges of $\sim 400\text{ nm}$. Crystalline cubes are shown in Fig. 2a,b. The spacing of $3.0\text{--}3.2\text{ \AA}$ [25] for the high-contrast region probably corresponds to the crystalline phase of $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ (Fig. 2a,b). Also TEM images show that amorphous Mn oxide is deposited on the surface of $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ nanoparticles (Fig. 2a,b).

For Mn oxide supported on Co_3O_4 irregular particles were observed (Fig. 2c,d). The spacing of $2.5\text{--}2.6\text{ \AA}$ for the high-contrast region may correspond to the (311) planes of Co_3O_4 [26] (Fig. 2c,d). HRTEM images show the Mn oxide phase, which is deposited on the surface of Co_3O_4 nanoparticles (Fig. 2c,d). The spacing of $7.0\text{--}8.0\text{ \AA}$ for the high-contrast region probably corresponds to the (100) [27] planes of the layered Mn oxide (Fig. 2c,d).

TEM images for Mn oxide supported on CuO show that amorphous Mn oxide is deposited on the surface of the nanoparticles (Fig. 2e,f).

For Mn oxide supported on Fe_3O_4 , the Fe_3O_4 particles have cubic morphology with edges of $\sim 200\text{ nm}$ (Fig. 2g,h). The spacing of $2.5\text{--}2.6\text{ \AA}$ for the high-contrast region probably corresponds to the (311) planes of Fe_3O_4 (Fig. 2g,h) [28]. HRTEM images show Mn oxide which is deposited on the surface of Fe_3O_4 nanoparticles (Fig. 2g,h).

HRTEM images for Mn oxide supported on MgO show amorphous Mn oxide (Fig. 2i,j). For Mn oxide supported on NiO , spherical NiO (diameter: $10\text{--}100\text{ nm}$) particles were

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